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EFFECT OF ORGANIC SUBSTANCES IN CLAY ROCKS ON FORMATION OF A BLACK CORE IN CERAMICS

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When clay rocks are heated, decomposition of organic substances is accompanied by liberation of H_2 , CO , and CO_2 , which creates the reducing character of the gas medium. Combustion of residual carbon takes place in the 250–500°C temperature region and is extremal in character due to diffusion of oxygen into the internal layers of the heat-treated material. To exclude a black core, holding in the 700–800°C region is recommended for completing combustion of oxygen and forming hollow articles with the minimum acceptable thickness of the external and internal walls.

Formation of a black core in fired ceramics is characteristic of all kinds of ceramic articles. This is especially true of large articles and rapidly fired tiles. It is believed that the cause of formation of a black core is carbon coke residue — the product of combustion of organic matter [1]. Indicating the incomplete physicochemical processes (partial decomposition of organic substances, insufficient oxidation of carbon) that take place in the core of ceramics, the black core is a source of salt formation during use of the articles.

In many regions of the country, up to 20% additives containing organic substances (sawdust, coal mining wastes) are added to the batch in production of ceramics to regulate the process characteristics of the paste and the performance properties of the fired material [2].

For this reason, studying the behavior of organic substances in clay rocks in heat treatment and development of process methods that exclude formation of a black core is of scientific and practical interest. Research in this direction will allow determining the qualitative and quantitative compositions of the products of decomposition of organic substances and establishing their role in sintering of ceramic pastes in more detail, as well as developing firing regimes and regulating structure formation and the properties of the articles obtained as a function of the quality of the raw material.

In studying the processes that take place in heat treatment of clay rocks, decomposition of organic substances with liberation of gaseous products has been inadequately in-

vestigated. This is not only due to the opinion concerning the secondary character of the effect of evolution of gas on sintering and structure formation in ceramics, but also the complexity of conducting the experiments [3].

The results of studying decomposition of organic substances (quantitative and qualitative compositions of the gases liberated, change in the residual carbon content) in heat treatment of clay rocks are reported below.

Low-melting Krasnoyarsk clay (Tyva Republic) was investigated. This clay rock is used for production of dense and porous ceramics. The slip made from this clay is distinguished by better liquescence, fluidity, lower thickening, and molded stock articles are less prone to deformation and crack formation. Most importantly, of local clay rocks, Krasnoyarsk clay is characterized by a high content of organic substances (0.81% in terms of dry carbon). The chemical composition of Krasnoyarsk clay is as follows (mass content, %): 56.63 SiO_3 , 15.13 Al_2O_3 , 0.97 TiO_2 , 6.30 Fe_2O_3 , 5.78 CaO , 2.85 MgO , 1.08 K_2O , 1.25 Na_2O , 0.87 SO_3 , 8.35 firing loss (FL). The refractoriness temperature of the clay is 1200°C.

X-ray phase analysis showed that montmorillonite is the basic rock-forming mineral in Krasnoyarsk clay and that an insignificant amount of hydromica is present. The contaminants are quartz, orthoclase, and goethite. In the granulometric composition, the proportion of argillaceous, dust-like, and sandy particles varies within the limits of 28–35, 38–52, and 18–26%.

The study was conducted with the following method. For the gas analysis, cylindrical samples 15 mm in diameter and height were dry molded at a pressure of 25 MPa from ground and dried clay. Heat treatment was conducted in a quartz tube

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TABLE 1

Firing temperature, °C	Volume content of gases, %				
	H ₂	CO	CO ₂	O ₂	N ₂
200	—	—	0.04	20.98	78.62
250	1.64	11.24	8.73	16.30	62.10
350	4.07	24.36	17.80	12.60	34.14
450	8.65	21.83	26.24	9.97	33.30
650	13.27	17.22	34.07	7.89	27.55
850	19.73	12.57	41.32	5.24	21.12
1050	21.33	8.41	46.14	4.04	20.05

25 mm in diameter and 200 mm long which was placed in a laboratory electric microfurnace attached to a MX-1323 mass spectrometer. During firing, the gas stream was fed into a special chamber of the mass spectrometer where it was ionized in vacuum conditions at a pressure of 10^{-5} Pa. The current strength in studying volatiles with different masses was used as a measure of the content of a given component in the gas analyzed.

The residual solid carbon content in the fired samples was determined on a Lekko unit. The essence of the analysis consists of the fact that the sample is burned in a high-frequency induction furnace together with flux (tin) with oxygen feed. The volatile combustion products (CO and CO₂) are automatically analyzed using molecular sieves. Then the amount of solid carbon is calculated based on the results of the volume content of the indicated gases. In Krasnoyarsk clay, the mass content of organic substances was 0.86% in terms of dry carbon.

Organic substances in clay rocks are in different forms and are represented by slightly decomposed organic residues of plant and animal origin [4]. Most of the organic substances are represented by humic acids which are in the adsorbed state on the surface of the clay particles.

Heat treatment of the experimental samples showed that decomposition and oxidation of organic substances began after 200°C, as the results of the gas analysis indicated (Table 1). After this temperature, the content of the basic components of the gas medium in the firing zone began to change. It should be noted that up to 200°C, the volume content of the basic gases nitrogen, oxygen, and carbon dioxide in air almost did not change and was 78, 62, 20, 98, and 0.03%, respectively.

It was found that intensive decomposition of organic substances took place in the 250–300°C temperature range, accompanied by liberation of hydrogen, carbon monoxide, and carbon dioxide. Here 1.64% H₂, 11.24% CO, and 8.73% CO₂ (volume content) were liberated from Krasnoyarsk clay. The data obtained confirm the conclusions of G. L. Stadnikov that when clays are heated, humic acids split some carboxyls with liberation of CO and CO₂ [5]. It should be noted that the character of the gaseous medium is reducing when the or-

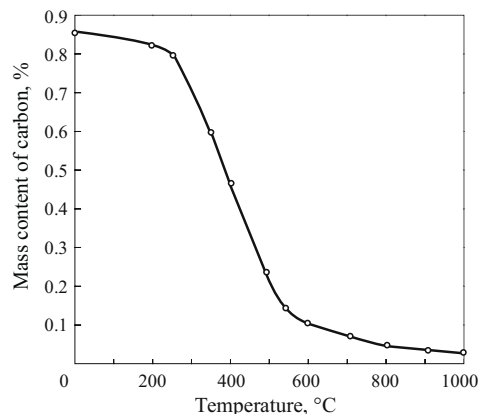


Fig. 1. Burnoff of carbon as a function of the firing temperature.

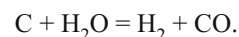
ganic substances begin to decompose, since the total volume content of active H₂ and CO gases is equal to 12.88%, which is two times higher than the minimum required content (6%) [1].

Due to decomposition of the organic substances and oxidation, the mass content of carbon in the samples fired at 250 and 300°C decreased to 0.80 and 0.71%, respectively (Fig. 1).

In the 250–350°C range, liberation of active gases intensified and the volume content of hydrogen reached 4.07% while the content of carbon monoxide attained 24.36%. The carbon dioxide content parallelly increased due to oxidation of carbon. The residual carbon content continued to decrease intensively and reached 0.57% at 350°C.

Decomposition of organic substances continued in the 350–450°C temperature segment. Despite the gradual increase in the proportion of hydrogen, liberation of carbon monoxide decreased to 21.83%. Nevertheless, the character of the gaseous medium remained strongly reducing (the total volume content of H₂ and CO was 30.48%). Oxidation of carbon continued with intensive liberation of carbon dioxide, which decreased the mass content to 0.34%.

During dehydration of clay minerals (450–650°C), the gaseous medium became even richer in hydrogen (up to 13.27%) and carbon dioxide (up to 34.07%), which was not only due to oxidation of carbon but also to decomposition of liberated chemically bound water with a carbon residue:



It was previously found in [6] that at 350–650°C, active forms of iron oxide are reduced in the inner layers of fired material with the participation of reducing gases and carbon with formation of carbon dioxide. The reduction of magnetite and wüstite by carbon monoxide, revealed by nuclear gamma-resonance spectroscopy, confirmed the increase in the amount of carbon dioxide in the gaseous medium. In the inner layers of the fired material where oxygen molecules did not penetrate, the carbon residues acted as reducing

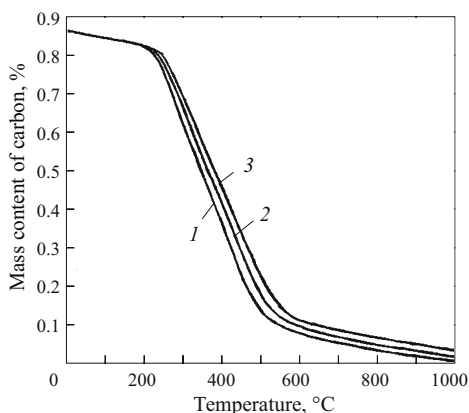


Fig. 2. Dynamics of combustion of carbon as a function of the molding method: 1) casting method; 2) plastic method; 3) semidry molding.

agents for wüstite. At 650°C, as a result of chemically bound water and iron compounds reacting with oxygen, the carbon content in the fired material decreased to 0.10%, which is 11.1% of the total initial solid carbon content.

The gaseous medium became rich in hydrogen (up to 21%) when the temperature was increased to 1050°C due to pyrolysis of molecules of chemically bound water in the high temperature region. The increase in the CO₂ content can be attributed to reduction of wüstite through CO with liberation of carbon monoxide and dissociation of carbonates. Despite the decrease in the proportion of carbon monoxide to 8.41%, the character of the gaseous medium remained strongly reducing.

The analysis of the character of the curve in Fig. 1 shows that oxidation and combustion of carbon slowed after 550°C, which can be explained by filling of pores with water vapors as a result of dehydration of clay minerals. The molecules of water separated complicate access of oxygen to the inner layers of the fired material by filling slit voids and small pores. Nevertheless, the mass content of carbon gradually decreased to 0.05% up to 1000°C.

It was found that intensive decomposition of organic substances in heating low-melting Krasnoyarsk clay and oxidation of deposited carbon took place in the 250–550°C region.

According to existing opinions, the mechanism of combustion of carbon is due to bulk diffusion of oxygen [4]. Combustion of carbon begins from the surface of the samples and moves into the depth of the material. This is confirmed by the data in Table 2, which shows the residual carbon content in different layers of fired material based on Krasnoyarsk clay at temperatures of 700–1000°C. The oxygen diffusion rate is determined by the concentration of oxygen in the surrounding gas medium and the external diffusion resistance of the adjacent layer.

It was found that the rate of decomposition of organic substances and combustion of carbon when Krasnoyarsk clay was heated to 600°C is extremal and then diffusion in character, i.e., the combustion rate is limited by the rate of diffusion of oxygen from the surrounding medium. An analysis of the mechanism of burnoff of the carbon shows that it is identical to the process of solid-phase reactions that limit the diffusion rate of a mobile reagent through a layer of the product of the reaction.

The dynamics and mechanisms of oxidation of residual carbon and consequently elimination of the black core of ceramics are a function of the raw materials and process and structural factors. If the effect of the raw materials (type and content of organic additives and substances) can be regulated with the firing parameters and conditions, then the process (molding methods) and design (application and size of the article) factors have the basic effect on formation and elimination of the black core.

The carbon combustion curves characterizing the dependence of the oxidation dynamics on the molding method are shown in Fig. 2. Decomposition of organic substances and combustion of carbon are most rapid in primary firing of majolica articles made in gypsum molds (4–5 mm thickness) from slip. Carbon burns off much more slowly in 50 × 50 × 5 mm tiles made from molding powder with a 10% moisture content molded at 40 MPa pressure. It was found that in firing of molded articles, decreasing the temperature elevation rate from 10 to 5 K/min after 700°C significantly reduced the mass content of residual carbon in the fired articles (from 0.06 to 0.030%).

Investigating the effect of the basic process factors on the kinetics of combustion of carbon will allow developing scientifically substantiated conditions for firing of ceramic articles. The optimum size for grinding clay rocks to decrease the carbon burnoff time is less than 0.5 mm.

To intensify combustion of carbon and correspondingly reduce the duration of the firing cycle, we recommend molding hollow articles with the minimum acceptable outer and inner wall thickness. In developing the firing conditions, it is necessary to provide for a decrease in the temperature elevation rate or holding in the 700–800°C region (in oxidizing medium) to complete combustion of carbon and dehydration of clay minerals before the liquid phase begins to form.

TABLE 2

Firing temperature, °C	Mass carbon content, %, in layer		
	surface	middle	inner
700	0.06	0.10	0.16
800	0.04	0.08	0.13
900	0.03	0.06	0.10
1000	0.02	0.04	0.07

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